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Chemistry 1
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 28
Introduction to Chemical Applications

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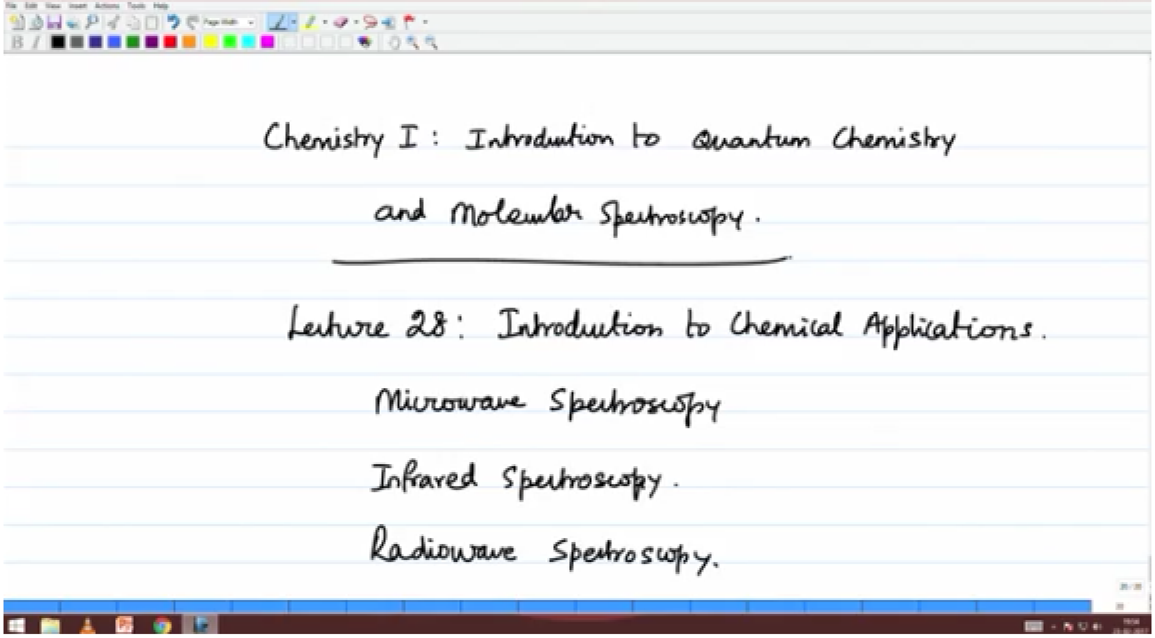

Chemistry I : Introduction to Quantum Chemistry and Molecular Spectroscopy.

Lecture 28 : Introduction to Chemical Applications.

Microwave Spectroscopy

Infrared Spectroscopy.

Radiowave Spectroscopy.

Welcome back to the lectures introductory quantum chemistry and molecular spectroscopy. From this lecture onwards till the end of the course we shall concentrate on elementary spectroscopy by request to you is that you recall the first three of 3 lectures if I remember during the first week in which I discussed elementary properties of the electromagnetic radiation. The electric field oscillation of the or the electric component of the electromagnetic field oscillating in space and time as well as the magnetic field which is perpendicular to the reckon of the electric field then also oscillating in space and time in that axis and both the oscillations of electric and magnetic field or perpendicular to the direction of propagation that was one of the lectures. And in the other lecture I told you that we are in general interested in the properties of the line positions, the line intensities and the line widths in practically all branches of spectroscopy.

Spectroscopy of course samples, the molecular properties and give us the fingerprints of molecular structures and various other things, and different branches of spectroscopy look at different things in the molecular domain. For example the optical domain corresponds to the three major spectroscopy branches that are others microwave spectroscopy, infrared and visible spectroscopy, UV visible spectroscopy and then x-ray spectroscopy.

Each region of the electromagnetic radiation in each spectral region that is a microwave domain region or the infrared region it gives us information about specific properties, then we use microwave radiation, we are able to sample the properties of molecular rotation and also the electric properties of the molecule such as the quadrupole moments and so on.

If we use infrared spectrum we are able to get the bond strengths, the bond lengths, the force fields percent in the molecule as well as the dissociation energies of the molecular systems and the vibrational information, the frequency of the vibrations all details associated with change in bond lengths, we get that from the infrared. And when we use electronic spectroscopy we are able to get the electronic transitions observed and they in a very limited domain lead to color which is what we see in the colorful spectrum of the visible light.

The magnetic domain for example, a study inducing both the radio wave region as well as the microwave region for studying the electronic magnetic moments associated with the electrons.

We'll do it bit of a quantitative assessment in this lecture today with some numbers and these are what are called the ball park numbers or they are also known as the back of the envelope calculations.

For those of you who do not understand what is meant by back of the envelope calculations I must give you an anecdote that, long before when you arrive or born internet was not obviously there and even emails where not there only postage and post office or some mail through normal delivery was the order of the day, when scientist declared new results to fellow scientist through postage very often the new results were checked by the receivers on the back of the empty envelope which was attached to them, and in that table do a small calculations and try to assess that it is indeed a new result that need friend or there communicator has been declaring, so if you recall we will just to do something very similar order of magnitude calculations or back of the envelope to 3 applications, 3 branches of spectroscopy that you see here namely microwave spectroscopy, infrared spectroscopy and radio wave spectroscopy, okay.

Let us look at the microwave spectroscopy to begin with, okay. Radiation frequency range if you remember is 10 to the, 10 hertz that is about 10 gigahertz to about 10 to the 12 hertz which is 1000 gigahertz or a terahertz, terahertz, okay, and this is for microwave. And microwave spectroscopy is used to study molecular rotations, and through molecular rotations the equilibrium structure of the molecule.
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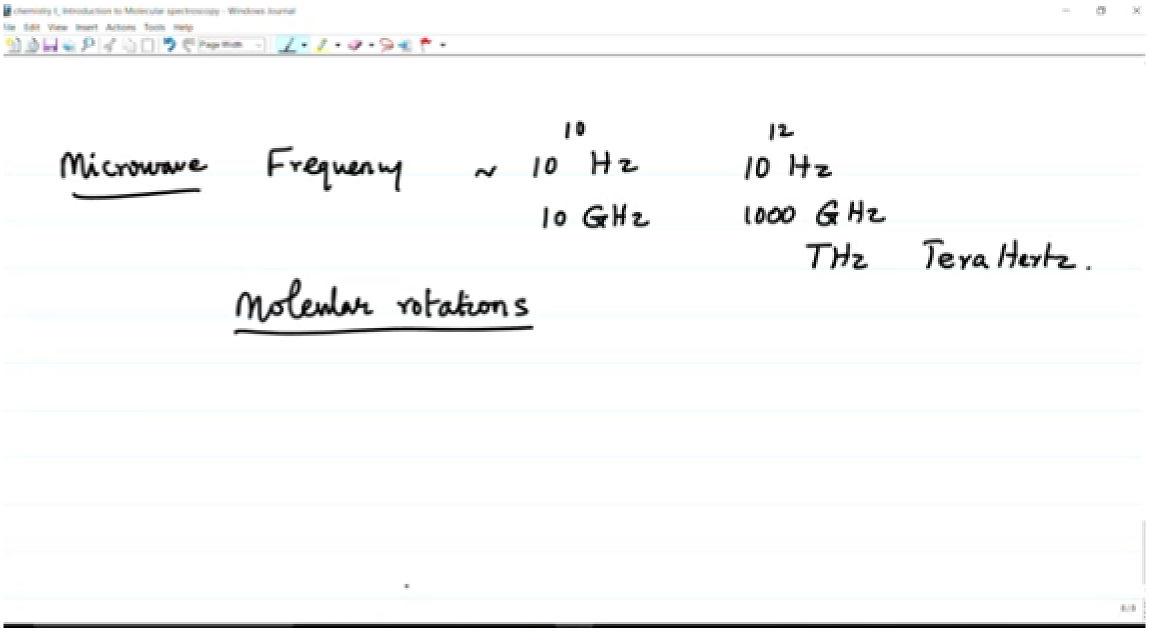

Microwave Frequency ~ 10^{10} Hz 10^{12} Hz

10 GHz 1000 GHz

THz Tera Hertz.

Molecular rotations

Now that means molecular rotational energies must be in the range of the frequency that you have here and the energy corresponding to this frequency which is given by is equal to H nu, which if you write is approximately 6.6 to the 10 is to -34 joule second times say 10 to the, 10 to the 12 hertz either one of these hertz which is basically second inverse, second inverse and for that goes away, so you are looking at the energy ranges between 6.6 x 10 to the -24 to 10 to the -22 joules, okay.

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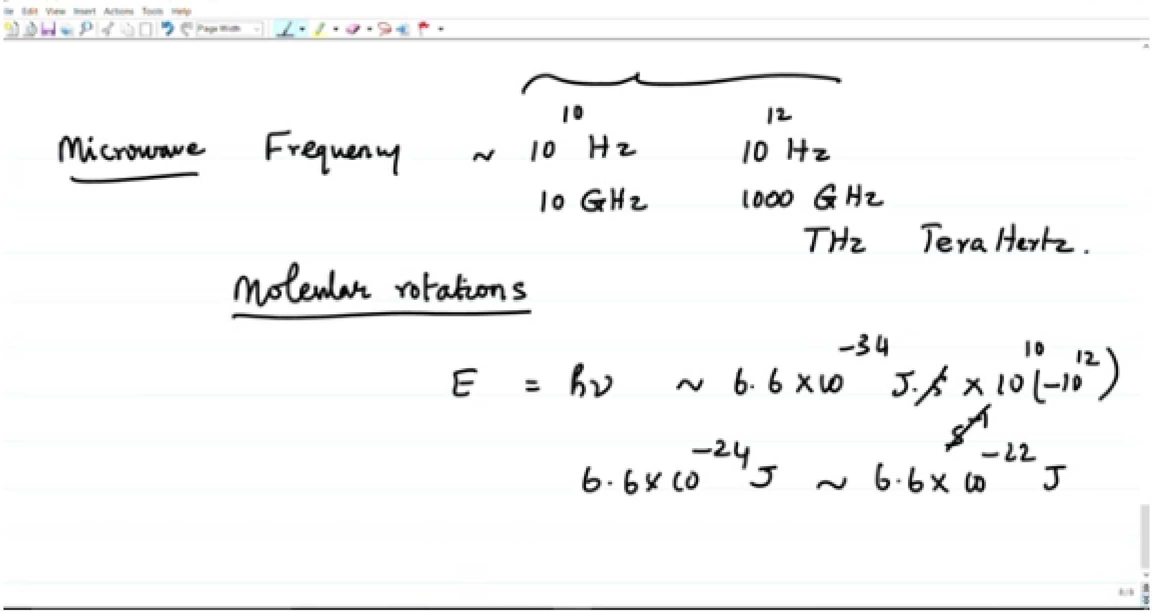

Microwave Frequency ~ $\overbrace{10^{10} \text{ Hz} \quad 10^{12} \text{ Hz}}$

10 GHz 1000 GHz

THz Tera Hertz.

Molecular rotations

$$E = h\nu \sim 6.6 \times 10^{-34}\ J.\cancel{s} \times 10^{10} (-10^{12})\ \cancel{s^{-1}}$$

$$6.6 \times 10^{-24}\ J \sim 6.6 \times 10^{-22}\ J$$

Now let us see the molecular rotations, classically rotational energy for a diatomic molecule if you have to consider about an axis suppose the diatomic molecule this M1, M2 and center mass you see here same about an axis which is perpendicular to the bond, because these are the two axis about which the moment of inertia of the molecule is nonzero in the point mass approximation, okay, so if we do that the molecular rotational kinetic energy is given by a simple expression it is given by J square/2I, where J is the angular momentum of the molecule which causes the rotation, and I is the moment of inertia of the molecule.

We will do these calculations more elaborately when we deal with microwave spectroscopy specially, but today's lecture is to give you roughly the magnitude and the scale, so if you are looking at the say for example carbon monoxide CO, the masses or let's do simple calculations carbon 12 and oxygen 16 then the moment of inertia I is given by mu R square where mu is the reduced mass of the molecule and R is the bond length, the distance between the carbon and oxygen, let's assume equilibrium, need not worry about exited states and so on, equilibrium if you do that then approximate masses for carbon-monoxide if you have to calculate you do this by 12 grams divided by the Avogadro number which is the atomic mass and 16 oxygen mass divided by the Avogadro number, please remember reduced mass is M1 M2/M1+M2 where you have seen M1 and M2 are the two masses that you have,

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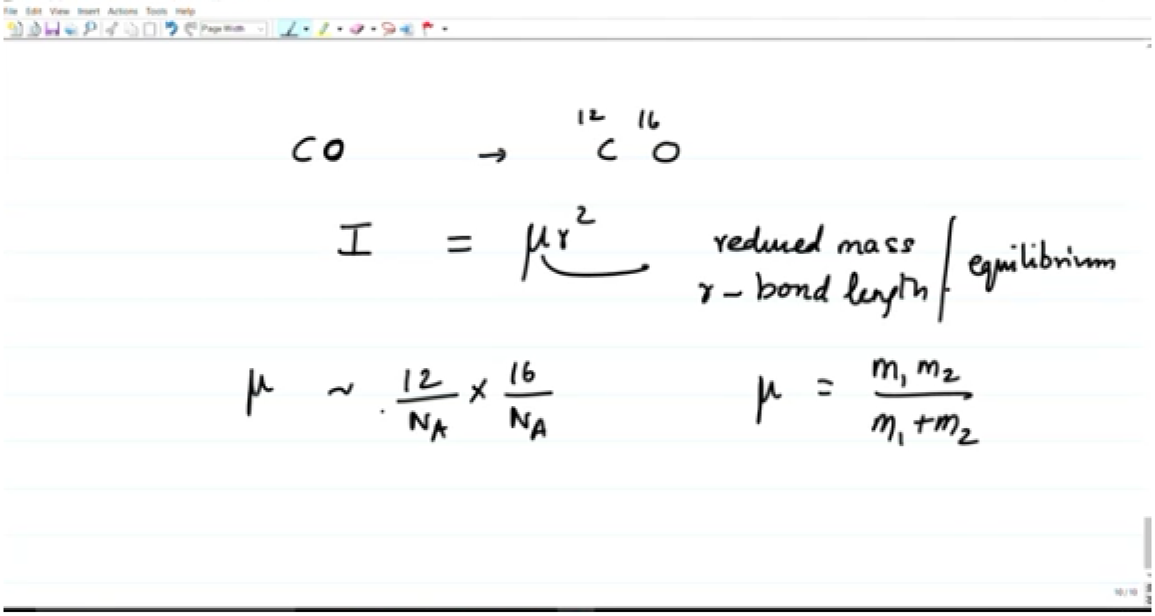

$$CO \rightarrow {}^{12}C\ {}^{16}O$$

$$I = \underbrace{\mu r^2}$$

reduced mass
r – bond length | equilibrium

$$\mu \sim \frac{12}{N_A} \times \frac{16}{N_A} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

so in this case mu is given by 12+16/NA, so you are looking at roughly 12 x 16/28 Avogadro number, this was the gram,

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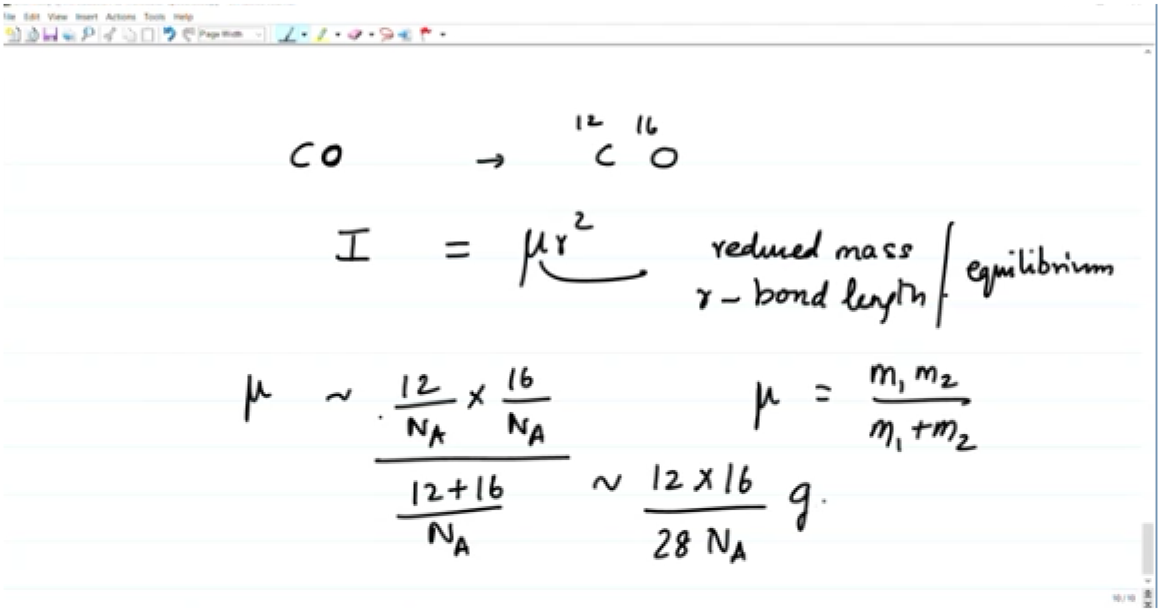

$$CO \rightarrow {}^{12}C\,{}^{16}O$$

$$I = \underbrace{\mu r^2}$$

reduced mass

r – bond length | equilibrium

$$\mu \sim \frac{\frac{12}{N_A} \times \frac{16}{N_A}}{\frac{12+16}{N_A}} \sim \frac{12 \times 16}{28\, N_A}\, g.$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

of course we reduced joules and the SI units we have to use, so mu is approximately 12 times 16 times 10 to the -3/28 x 10 to the minus, NA is 10 to the 23 x 6 point something, let's keep it as 6.02 to a 6 point, so let's do simple calculation.

You have 2, and 2 x 16, 32/28 roughly keep it as 1, you were looking at 10 to the -26 kilogram, okay,

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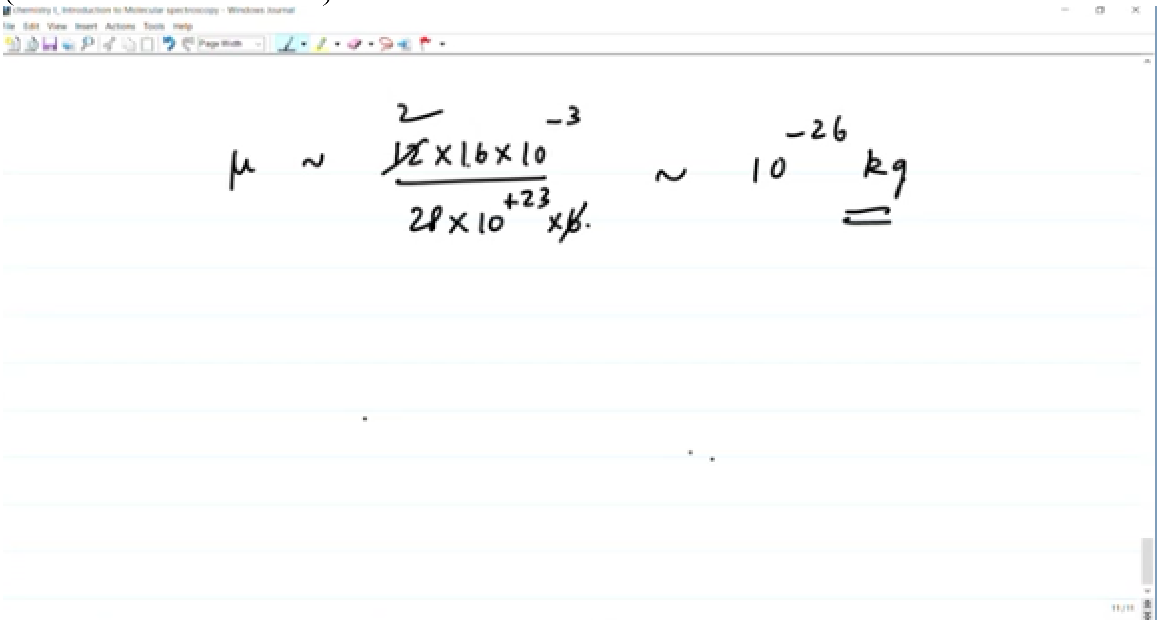

$$\mu \sim \frac{\overset{2}{\cancel{12}} \times 16 \times 10^{-3}}{2\cancel{8} \times 10^{+23} \times \cancel{6}} \sim \underline{\underline{10^{-26}\ kg}}$$

order of magnitude that's what you were looking at, and that's mu or let's assume that to the bond length is somewhere between 1 and 1.2 angstroms and even if we keep 1 angstroms, okay, that's 10 to the -10 meters, therefore I which is mu R square is approximately 10 to the -26 kilogram times, 10 to the -10 square meter square kilogram meter square which is about 10 to the -46 kilogram meter square, this is the moment of inertia.

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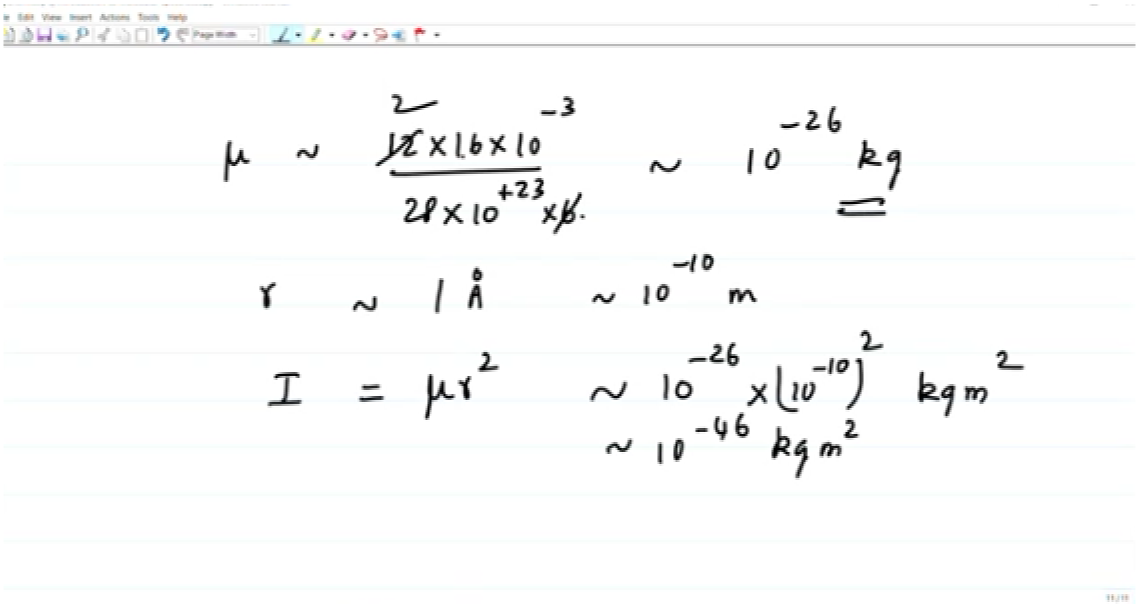

$$\mu \sim \frac{\overset{2}{\cancel{12}} \times 16 \times 10^{-3}}{28 \times 10^{+23} \times \cancel{6}} \sim 10^{-26}\ \underline{\underline{kg}}$$

$$r \sim 1\ \mathring{A} \sim 10^{-10}\ m$$

$$I = \mu r^2 \sim 10^{-26} \times (10^{-10})^2\ kg\,m^2$$

$$\sim 10^{-46}\ kg\,m^2$$

Now angular momentum for molecules J or usually given in the units of H bar, namely H/2 pi and H is Planck's constant, so even if we take the lowest volume for the angular momentum nonzero value H bar into some value M and so let's choose M to be 1, meaning that was the really lowest rotational energy, if you do that H/2 pi is again 6.6/2 pi times 10 to the -34 joules second is approximately 10 to the -34 joules second, okay, 2 pi is 6.128 or whatever, so it's about 1.

So let's do the energy calculation now E as J square/2I you can see that it is 10 to the -48, sorry 10 to the -68, it's joule square second square so let me write the actual units kilogram meter square per second whole square divided by 2I and if you recall the I, I is about 10 to the -46 kilogram meter square, so it gives you about 10 to the -22 kilogram meter square per second square which is the joule,

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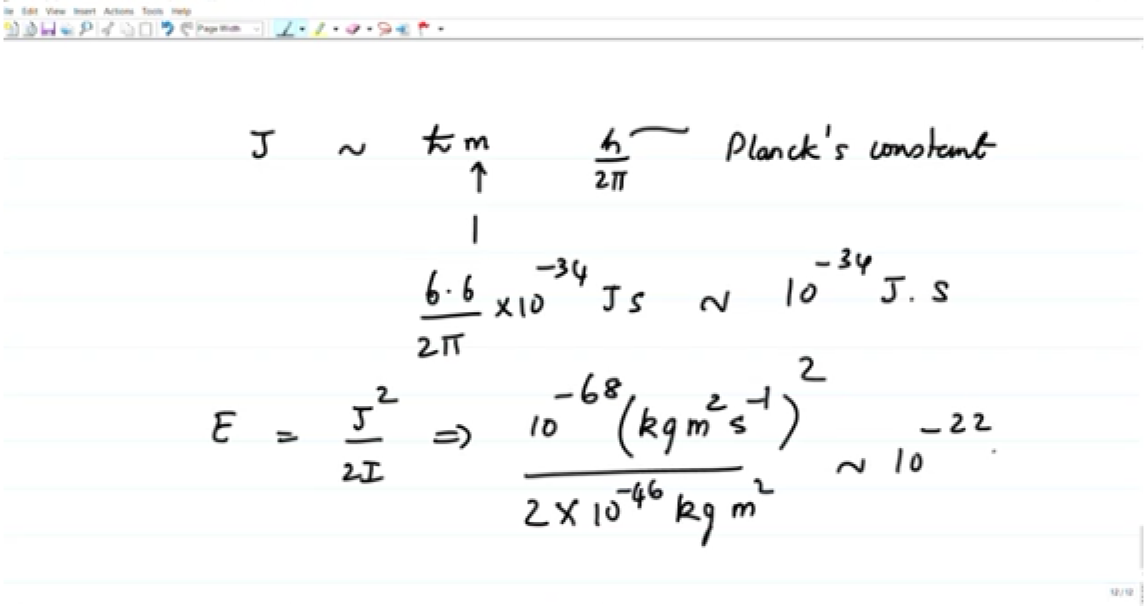

$$J \sim \hbar m \qquad \frac{h}{2\pi} — \text{Planck's constant}$$

$$\overset{\uparrow}{1}$$

$$\frac{6.6}{2\pi} \times 10^{-34}\ Js \sim 10^{-34}\ J.s$$

$$E = \frac{J^2}{2I} \Rightarrow \frac{10^{-68}\,(kg\,m^2 s^{-1})^2}{2 \times 10^{-46}\ kg\,m^2} \sim 10^{-22}$$

okay, therefore the rotational energy is of the order for a molecule, 10 to the -22 joules, and if you compare this with the frequency of electromagnetic radiation that is in this range you know that's H nu and that is 6.6 x 10 to the -34 times nu, you see nu immediately falls in the range of 10 to the 12 hertz, 10 to the 11 hertz,

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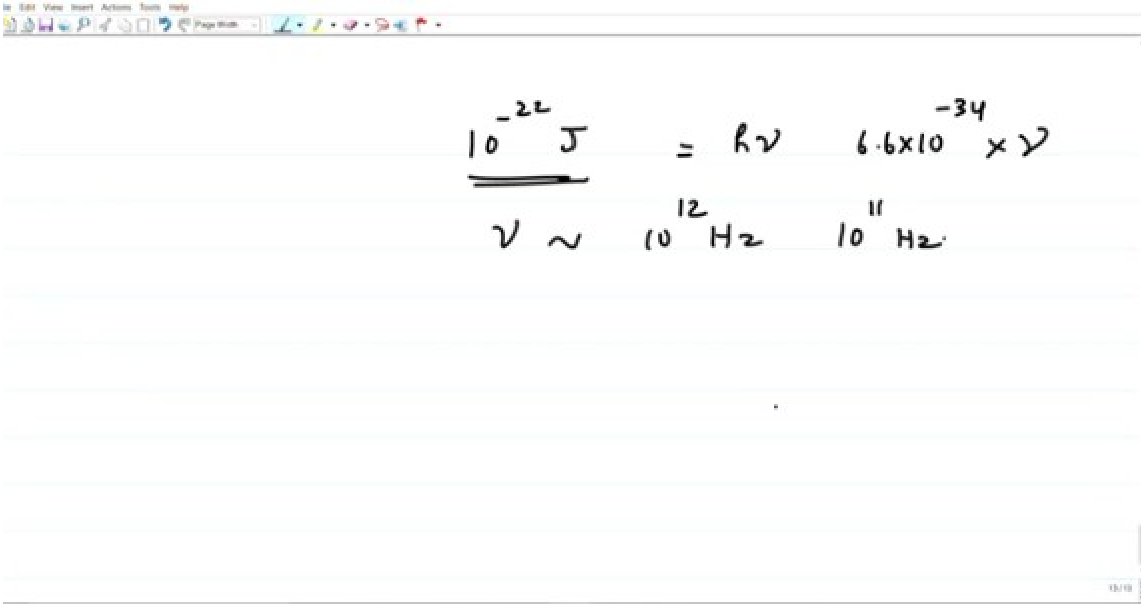

$$\underline{\underline{10^{-22}\ J}} = h\nu \quad 6.6\times 10^{-34} \times \nu$$

$$\nu \sim 10^{12}\ Hz \quad 10^{11}\ Hz$$

so the result is that a simple diatomic molecular rotation for an elementary molecule such as carbon-monoxide, the rotational energy levels if they are given by this order namely 10 to the -22 joules per molecule, the transitions between the rotational energy since of that order and that corresponds to an electromagnetic radiation whose frequency falls in the range of the 10 gigahertz to about a 1000 gigahertz, that's the reason why we say that microwave spectroscopy probes molecular rotations and molecular rotations involved in moment of inertia, and the moment of inertia is of course based on mu R square, so there is a bond length information, so if you extend to this to your triatomic or a polyatomic molecule and you want to study the geometry more in detail or more elaborately of course that's the part of microwave spectroscopy which we will look at more carefully, but the ball park figure is gigahertz to 1000 of gigahertz up to in that range is when you can study the molecular rotations.

Now the second one is about molecular vibrations and visible spectroscopy namely infrared visible spectroscopy, here we will go back in the reverse direction, let's assume molecular bond energies, chemical bond energies not weaker bonds namely ionic and covalent bond energies, so strong bond energies or usually between 50 kilo calories per mole to about 100 kilo calories per mole.

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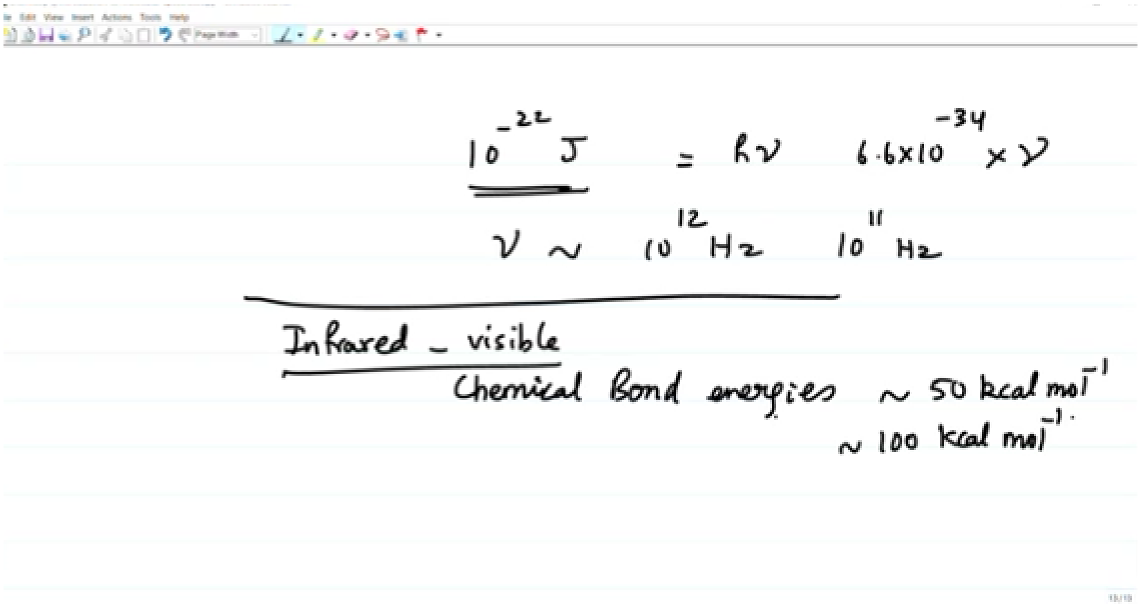

10^{-22} J $= h\nu$ $\quad 6.6\times10^{-34}\times\nu$

$\nu \sim 10^{12}$ Hz $\quad 10^{11}$ Hz

Infrared _ visible

Chemical Bond energies $\sim$ 50 kcal mol^{-1}

$\sim$ 100 kcal mol^{-1}.

And the mole is of course an Avogadro number of molecules, so if you are looking at energy, bond energy per molecule, let's assume 100 and 100 by the Avogadro number 6 x 6.022, but 6 x 10 to the 23, so you are looking at about 16, 1.6 times 10 to the -22 joules, this is kilo calories multiplied by 4.18 so you are looking at approximately 4 x 16, it's about 6 x 10 to the -22 joules, okay, that's for the, oh that is also an order of magnitude missing,

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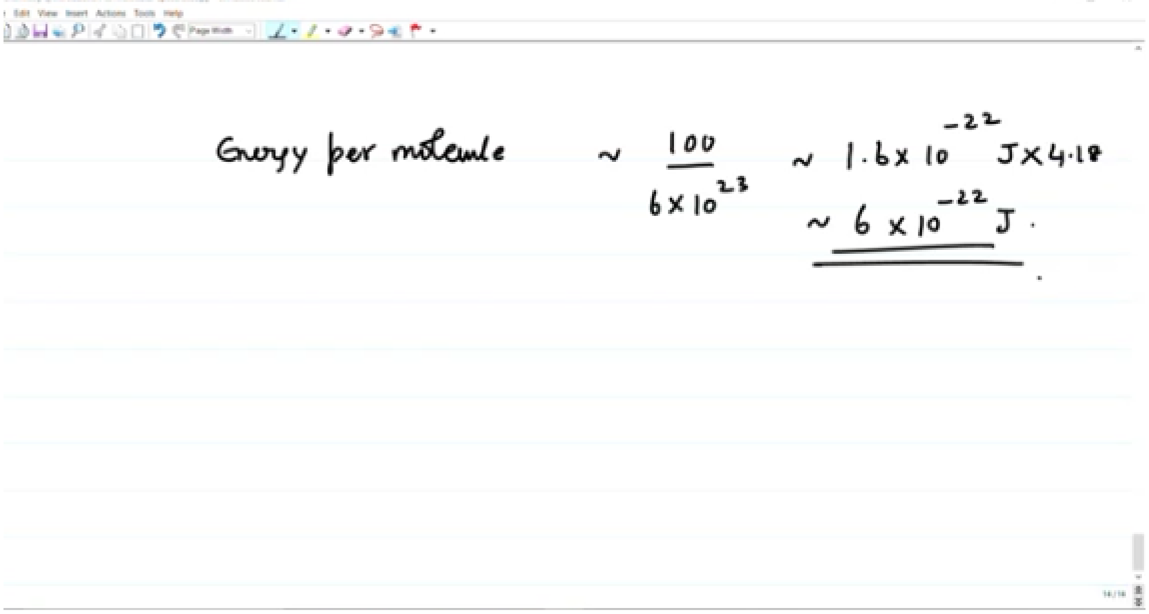

Energy per molecule $\sim \dfrac{100}{6\times10^{23}} \sim 1.6\times10^{-22}$ J$\times 4.18$

$\sim \underline{6\times10^{-22}}$ J.

it's 100 kilocalories therefore you multiply by 10 to the 3 and so you multiply this by 10 to the 3, 10 to the 3 so you get about 10 to the -19 joules, this is the energy per molecule due to the bond length or receive that much energy you have to provide

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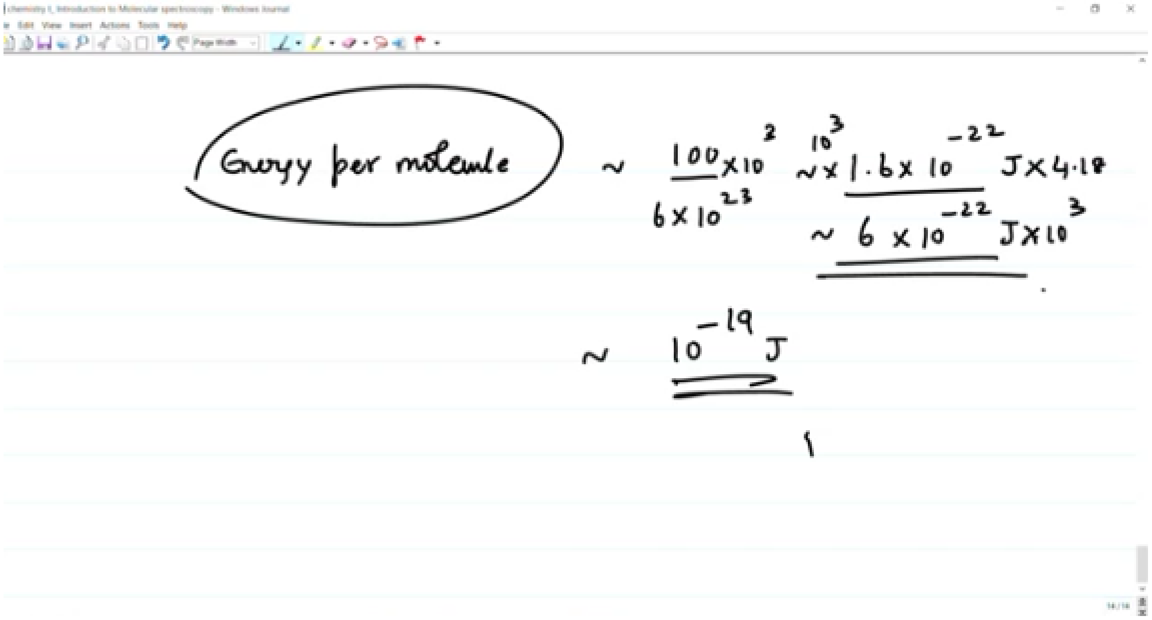

Energy per molecule $\sim \frac{100\times 10^{2}}{6\times 10^{23}} \overset{10^{3}}{\sim} \times \underline{1.6\times 10^{-22}}$ J$\times 4.18$

$\sim \underline{6\times 10^{-22}}$ J$\times 10^{3}$

$\sim \underline{10^{-19}}$ J

if you want the molecular vibrations or molecular energies to lead to bond breaking or excitation between different vibrational energies which should be a fraction of this, okay.

Now what is this correspond to in terms of the spectroscopic energies? So if this energy 10 to the -19 is to be equator to your radiation frequency nu whose energy is H nu, then you see immediately that this is 10 to the -34 times 6 and so you see that into nu, and also nu falls in the range of 10 to the +14 to 10 to the 15 hertz, you see 10 to the -19 = 6 times 10 to the -34 times nu, so you see that nu comes to this order,

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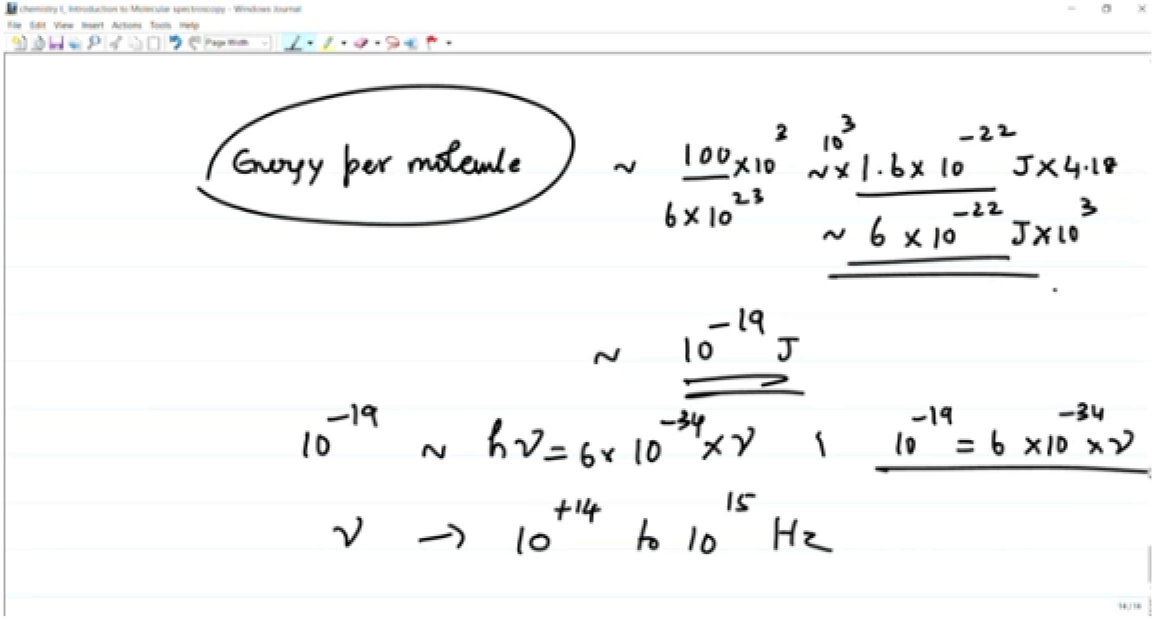

Energy per molecule $\sim \frac{100\times 10^{2}}{6\times 10^{23}} \overset{10^{3}}{\sim} \times \underline{1.6\times 10^{-22}}$ J$\times 4.18$

$\sim \underline{6\times 10^{-22}}$ J$\times 10^{3}$

$\sim \underline{10^{-19}}$ J

$10^{-19} \sim h\nu = 6\times 10^{-34}\times\nu$ $\quad$ $\underline{10^{-19} = 6\times 10^{-34}\times\nu}$

$\nu \rightarrow 10^{+14}$ to 10^{15} Hz

therefore molecular bonds are perturbed or excitation between vibrational energy states of a molecule can happen if you are looking at the order of energies of 10 to 100 kilo calories per mole that corresponds to frequency of radiation of the order of 10 to the 14 to the 10 to the 15

hertz, and 10 to the 14 hertz is 100 terahertz, and 10 to the 15 is 1000 terahertz therefore that’s the range and this frequency is typically, the frequency of radiation of infrared light,
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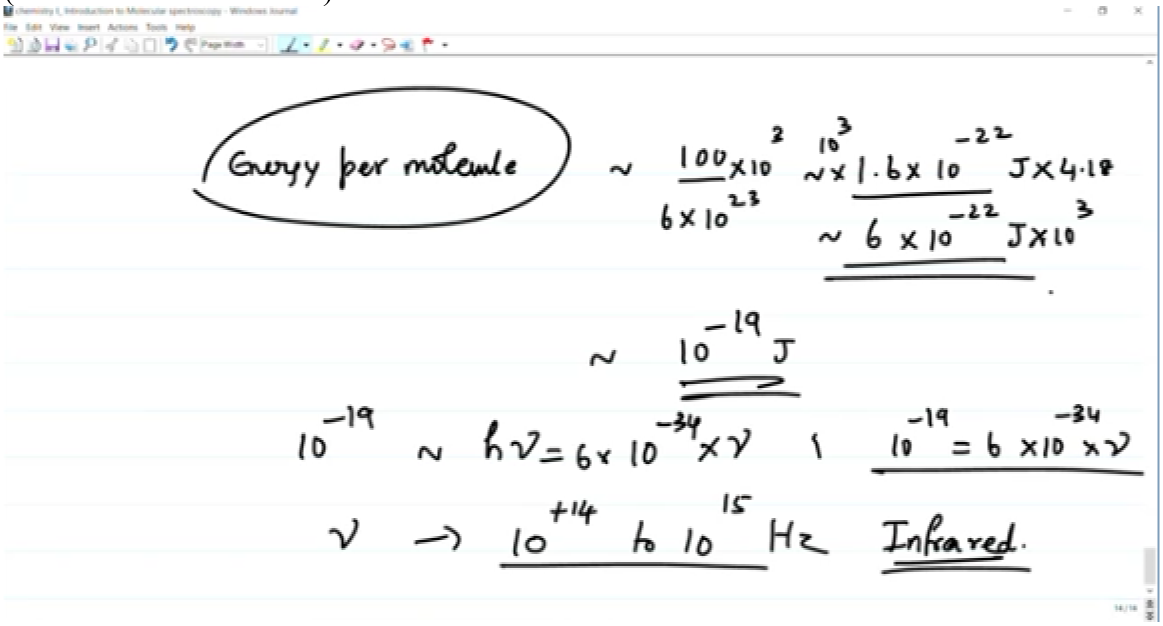

Energy per molecule

$$\sim \frac{100\times 10^{2}}{6\times 10^{23}} \overset{10^{3}}{\sim} \times \underline{1.6\times 10^{-22}}\ \mathrm{J}\times 4.18$$

$$\sim \underline{\underline{6\times 10^{-22}}}\ \mathrm{J}\times 10^{3}$$

$$\sim \underline{\underline{10^{-19}}}\ \mathrm{J}$$

$$10^{-19} \sim h\nu = 6\times 10^{-34}\times \nu \qquad \underline{10^{-19} = 6\times 10^{-34}\times \nu}$$

$$\nu \to \underline{10^{+14}\ \text{to}\ 10^{15}}\ \mathrm{Hz} \qquad \underline{\underline{\text{Infrared.}}}$$

therefore infrared spectroscopy or vibrational spectroscopy is studied using radiation of this order because this order of energy is commensurate to the molecular energy level changes due to vibrational motion or due to electronic excitation, if you have to supply the whole molecular energy it may go towards a slightly higher level of energy and that’s visible spectroscopy which creates, obviously which leads to what is called bond dissociation and things like that, you are familiar with organic chemistry details of photo chemical processes light induced to dissociation and so on, so visible and infrared spectroscopy fall in this range of 10 to the 14 to 10 to the 18 hertz, leading to molecular bond dissociation.

Now the last one that you want to look at is a very very low energy, but it’s a magnetic phenomenon. So magnetic moments of nuclei or tabulated for a large number of molecules and they are given by a factor, a property known as the gyromagnetic ratio, and it’s usually written by symbol gamma, this is gamma not nu and the molecular moment, the atomic or nuclei magnetic moment is given by gamma H bar I, gamma is obviously of the order of 10 to the 6 to 10 to the 7 hertz per magnetic field, unit magnetic field which this usually it is reported as per Tesla, T is Tesla and that is 10,000 gauss that’s a magnetic field.
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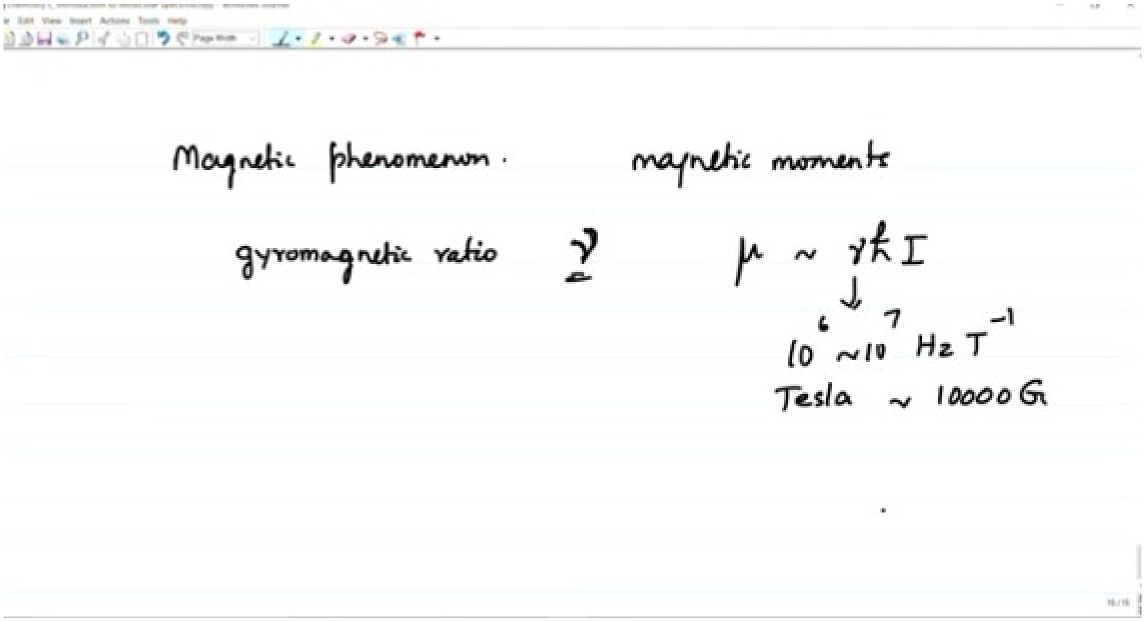

Magnetic phenomenon. magnetic moments

gyromagnetic ratio $\underline{\gamma}$ $\mu \sim \gamma \hbar I$

$\downarrow$

$10^{6} \sim 10^{7}$ Hz T^{-1}

Tesla $\sim$ 10000 G

Magnetic phenomena are explored by a static magnetic field which allows the magnetic moment to have multiple energy levels, and we will see that more in detail than we study magnetic resonance spectroscopy, but we're only looking at the order of magnitude of what kind of energies are involved, so if you are looking at nuclei with a gyromagnetic ratio of this order 10 to the 6 for example hertz per tesla then the magnetic moments or approximately this multiplied by the 6 x 10 to the -34 joules and the quantum number I is usually 0, one half 0 is not very useful to us,

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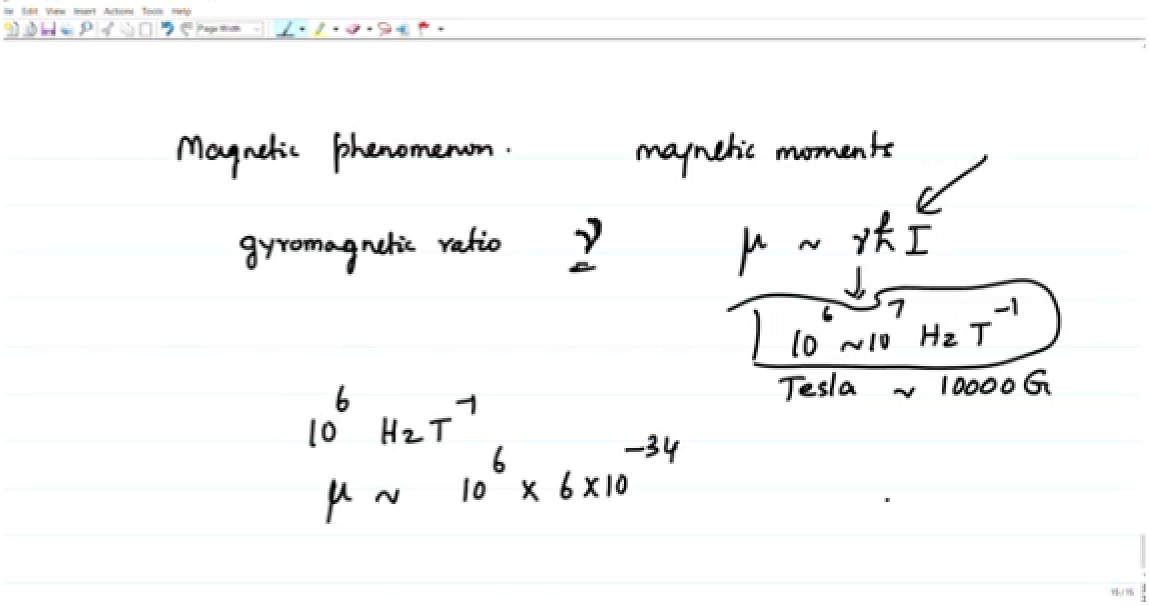

Magnetic phenomenon. magnetic moments

gyromagnetic ratio $\underline{\gamma}$ $\mu \sim \gamma \hbar I$

$\downarrow$

$10^{6} \sim 10^{7}$ Hz T^{-1}

Tesla $\sim$ 10000 G

10^{6} Hz T^{-1}

$\mu \sim 10^{6} \times 6 \times 10^{-34}$

one half, one three half and two and so on these are properties we'll study, so even if you assume one half as the spin quantum number associated with the nucleus you are looking at energy ranges between energy levels which correspond to your half configuration and the minus half configuration, so you are looking at energy delta E of the order of gamma H bar, H naught which is the field because the magnetic moment will interact with the field to have a certain energy and that energy is either corresponding to the half quantum number orientation of a proton nucleus or a minus half orientation of a proton nucleus.

For you I'm looking at energies of this order gamma, H bar, H naught, and so if you have 1 tesla field and your previous values of gamma H bar, H naught is approximately 10 to the 6, 10 to the -34, so you're about 10 to the -27 joules I believe, this is hertz per tesla, H is not, so the energies of the order of that 10 to the -27 joules, and this obviously corresponds to your frequency H nu, the energy is H nu the frequency nu, and this is 10 to the -34 so you see nu is of the order of 10 to the 7 hertz, okay, therefore magnetic phenomena,

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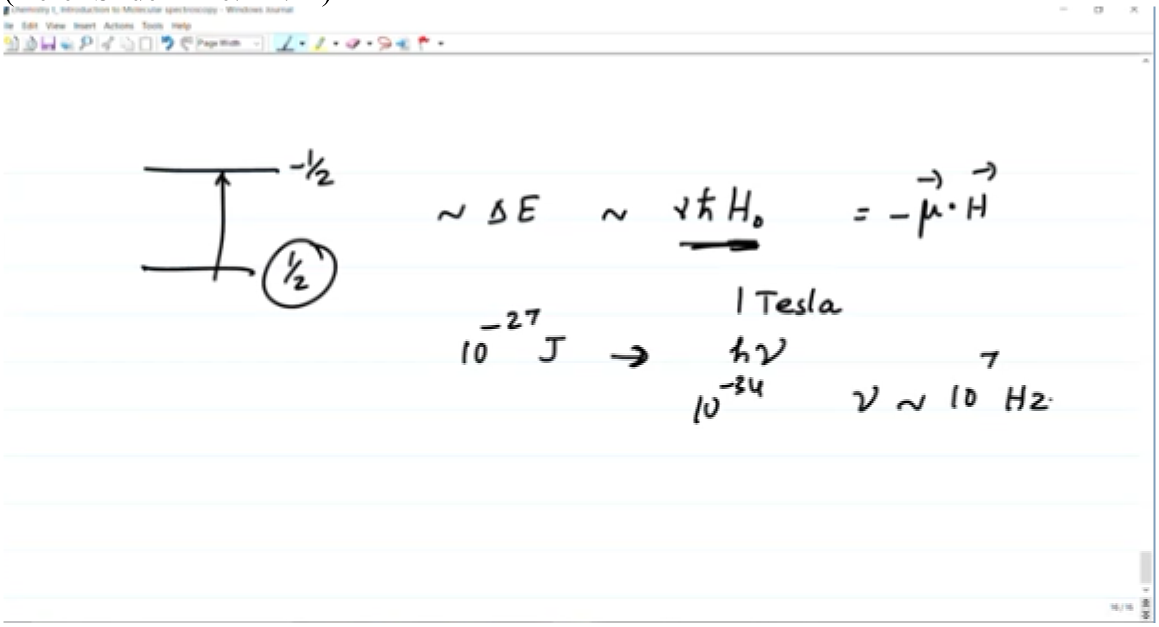

$\sim \Delta E \sim \underline{\gamma \hbar H_0} = -\vec{\mu}\cdot\vec{H}$

1 Tesla

$10^{-27}\,J \rightarrow \hbar\nu$

10^{-34} $\nu \sim 10^{7}$ Hz.

magnetic moments and the detection of nuclear magnetic moments and transitions that happen in the nuclear energy levels due to the, energy levels of the nucleus in a magnetic field is of the order of a megahertz, 10 to 100 megahertz for a field of about 1 tesla, therefore radio wave frequency, radio waves have that trend of frequency, megahertz frequency, radio waves are obviously the appropriate tools and to the magnetic, the oscillating magnetic field of the radio waves corresponds to frequencies of this order, so when you talk about chemical applications of spectroscopy to various fields one must have a priori some information and some knowledge about what's the order of magnitude energies involved, so I have given this only by giving you 3 simple examples, but as we see more and more individual techniques of spectroscopy we will see these things in detail, and also much more quantitatively, but you have to have an appreciation of which phenomena that you would be normally interested in when you study, your certain type of spectroscopy, this was categorized in the previous lecture but now with a bit of elementary details, I've also demonstrated that microwave spectroscopy studies rotational motion, vibrational spectroscopy studies bond strengths and bond information, and magnetic resonance spectroscopy studies magnetic moments of nuclei and therefore the chemical phenomena which are relevant to that. Thank you very much.

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